

(12) Patent Publication (B1)

(19) Japan Patent Office (JP)	(11) Patent Number: Patent No. 3263065
(43) Date Published: March 4, 2002	(24) Date of Registration: December 21, 2001
(51) Int. Cl. ⁷ C11D 7/30 C23G 5/028 H01L 21/304	ID Mark FI C11D 7/30 C23G 5/028 H01L 21/304 647 647A
Number of Claims: 1 (total of 12 pages)	
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Application subjected to Accelerated Examination	(74) Agent: 100071283 Patent Attorney ISSHIKI, Kensuke (and three others)
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(56) References: JP 6-220494 (JP, A) JP 11-50097 (JP, A) JP 9-111032 (JP, A) JP 5-140592 (JP, A) JP 5-156292 (JP, A) WO 00/56833 (WO, A1)	Continued to last page

(54) [Title of Invention] SOLVENT COMPOSITION FOR CLEANING

(57) [Scope of Claim]
[Claim 1] A solvent composition for cleaning including:
(a) 30 through 70 wt% of 1,1,1,3,3-pentafluorobutane; and
(b) 30 through 70 wt% of one kind of solvent or a mixed
solvent including at least two kinds of solvents selected from
among nitromethane, nitroethane, d-limonene, and

3-methoxybutyl acetate.
[Detailed Description of Invention]

[0001] [Technical Field to which the Invention Belongs] The present invention relates to a solvent composition for cleaning that contains 1,1,1,3,3-pentafluorobutane as a main ingredient and particularly relates to an art of improving the cleaning ability thereof.

[0002] [Conventional Art] Conventionally, chlorine-based solvents and fluorine-based solvents have been widely used as, for example, flux cleaners, solvents for dry cleaning, degreasing cleaners, buffing cleaners, resist removing agents, or solvents for removing adhesion water. However, chlorine-based solvents are substances causing groundwater pollution, and fluorine-based solvents are substances causing ozone layer depletion; because of their environmental problems, the use thereof is becoming restricted. Therefore, there is a demand from various fields for a new solvent that would take place of the above-mentioned solvents.

[0003] 1,1,1,3,3-pentafluorobutane (365mfc, chemical formula: C₄H₉F₅) is one such solvent (see, for example, Japanese Patent Application laid-open Publication No. 5-171189, Japanese Patent Application laid-open Publication No. 5-171190, Japanese Patent Application laid-open Publication No. 6-322394, or Japanese Patent Application laid-open Publication No. 7-168700). 1,1,1,3,3-pentafluorobutane has superior characteristics in that it does not include chlorine in its molecular structure, its ozone depletion potential (ODP) is zero, it is low in toxicity, its global warming potential (GWP) is also small, and thus it is ecological and clean.

[0004] [Issues to be Addressed by the Invention] However, 1,1,1,3,3-pentafluorobutane (365mfc) has a problem in that its KB value (kauri-butanol value) is approximately 14, which is extremely low, and that it almost has no degreasing ability. If the KB value is low, it will not be possible to exert sufficient cleaning ability required of various kinds of cleaners.

[0005] Therefore, proposals have been made to increase the cleaning ability by mixing, to 1,1,1,3,3-pentafluorobutane, methylene chloride or 1,1-dichloro-1-fluoroethane (HCFC-141b), which have a higher KB value and degreasing-cleaning ability than the above (see publications Japanese Patent Application laid-open Publication No. 5-171183 and Japanese Patent Application laid-open Publication No. 11-152236).

[0006] However, since methylene chloride is highly toxic, there are concerns about its negative influence on the human body during execution of work. Therefore, use thereof is not only preferable, but it is becoming harder to use. Further, 1,1-dichloro-1-fluoroethane (141b) has a high ozone depletion potential and in the future, it may be restricted under regulations.

[0007] The present invention has been made in view of such circumstances, and an object thereof is to provide a solvent composition for cleaning that contains 1,1,1,3,3-pentafluorobutane as a main ingredient and is superior in cleaning ability, and particularly, in degreasing-cleaning ability.

[0008]

[Means for Resolving the Issue] A solvent composition for cleaning according to the present invention for achieving such an object is characterized in including: (a) 30 through 70 wt% of 1,1,1,3,3-pentafluorobutane; and (b) 30 through 70 wt% of one kind of solvent or a mixed solvent including at least two kinds of solvents selected from among nitromethane, nitroethane, d-limonene, and 3-methoxybutyl acetate.

[0009]

[0010]

[0011]

[0012]

[0013]

[0014]

[0015]

[0016] Nitromethane, nitroethane, d-limonene, and 3-methoxybutyl acetate are such solvents found by the present inventor as to be suitable for increasing the cleaning ability of 1,1,1,3,3-pentafluorobutane. These have sufficient degreasing-cleaning abilities.

[0017] 1,1,1,3,3-pentafluorobutane is set to 30 through 70 wt%, and one kind of solvent or a mixed solvent including at least two kinds of solvents selected from among nitromethane, nitroethane, d-limonene, and 3-methoxybutyl acetate is set to 30 through 70 wt% because, if the content of the latter is too small, the increase in the cleaning ability is not so sufficient, and thus it is not possible to obtain a sufficient cleaning effect, whereas if the content of the latter is too large, the characteristics of nitromethane, nitroethane, d-limonene, and 3-methoxybutyl acetate will become too significant, and it will not be possible to take full advantage of the superior features of 1,1,1,3,3-pentafluorobutane.

[0018]

[Embodiment of the Invention] An embodiment of a solvent composition for cleaning according to the present invention will be described below. The solvent composition for cleaning according to the present invention includes: (a) 30 through 70 wt% of 1,1,1,3,3-pentafluorobutane; and (b) 30 through 70 wt% of one kind of solvent or a mixed solvent including at least two kinds of solvents selected from among nitromethane, nitroethane, d-limonene, and 3-methoxybutyl acetate. Other than this, it is possible to achieve compositions that are superior in cleaning ability, as with the present invention, with the following two types of solvent compositions for cleaning.

[0019] [1] A solvent composition including: (a) 30 through 80 wt% of 1,1,1,3,3-pentafluorobutane; and (b) 20 through 70 wt% of normal propyl bromide and/or isopropyl bromide.

[0020] [2] A solvent composition including: (a) 27 through 80 wt% of 1,1,1,3,3-pentafluorobutane; (b) 20 through 70 wt% of normal propyl bromide and/or isopropyl bromide; and (c) 3 through 15 wt% of one kind of solvent or a mixed solvent including at least two kinds of solvents selected from among alkanes with a carbon number of 5 or more, cycloalkanes with a carbon number of 5 or more, or alcohols.

[0021]

[0022] Normal propyl bromide (avnonyl n-propyl bromide; 1-bromopropane, referred to simply as NPB below) and isopropyl bromide (avnonyl isopropyl bromide; 2-bromopropane, referred to simply as IPB below) have been found to be solvents that are suitable for increasing the cleaning ability of 1,1,1,3,3-pentafluorobutane. NPB and IPB have a relatively high KB value of 125 and are superior in degreasing and cleaning. Further, as with 1,1,1,3,3-pentafluorobutane, they are nonflammable and have incombustible or flame-resistant characteristics and are therefore not classified as hazardous materials and are safe and easy to handle, and they have superior characteristics in that they do not include chlorine or fluorine in their molecular structures, their ozone depletion potential (ODP) and their global warming potential (GWP) are also small, and thus they are ecological and clean. By mixing NPB and/or IPB, which are high in KB value, to 1,1,1,3,3-pentafluorobutane, it is possible to achieve a significant increase in cleaning ability, and particularly, degreasing-cleaning ability, and thus, it is possible for the solvent to exhibit sufficient performance as various types of cleaners. Further, as with

conventional cases, it is nonflammable and thus is not classified as hazardous material and is safe and easy to handle. Further, its ozone depletion potential (ODP) and global warming potential (GWP) are also small, and thus, it is ecological and clean. 1,1,1,3,3-pentafluorobutane is set to 30 through 80 wt% and NPB and/or IPB is set to 20 through 70 wt% because if the content of NPB and/or IPB is too small, then the cleaning ability will not be increased that much and a sufficient cleaning effect cannot be obtained. Further, if the content of NPB and/or IPB is too large, then the characteristics of NPB and/or IPB will become too significant and dissolvability will become too large, and it will not be possible to take full advantage of the superior features of 1,1,1,3,3-pentafluorobutane. By ensuring at least 30 wt% in content of 1,1,1,3,3-pentafluorobutane, its characteristics can be exhibited. Further, at least one kind of solvent selected from alkanes with a carbon number of 5 or more, cycloalkanes with a carbon number of 5 or more, or alcohols is mixed in order to ① reduce the content of 1,1,1,3,3-pentafluorobutane, and ② to dissolve water-soluble inorganic substances etc. contained in flux etc. that cannot be sufficiently dissolved by normal propyl bromide and/or isopropyl bromide. 1,1,1,3,3-pentafluorobutane is extremely expensive and may give rise to a significant increase in cost if it is used in large quantities, and therefore, by mixing the solvents described above, which are much inexpensive, as a substitute, it is possible to avoid a significant increase in cost. The content of these solvents is set to 3 wt% or more in order to sufficiently dissolve the water-soluble inorganic substances etc. contained in flux etc. Further, the content of these solvents is set to 15 wt% or less because if too much of these solvents are mixed, the solvent composition will be turned into a combustible since these solvents are flammable and are classified as hazardous materials. As regards normal propyl bromide (NPB) and isopropyl bromide (IPB), either one may be blended individually, or both may be blended. Further, since NPB and IPB are likely to cause metal reaction with aluminum, its alloys, etc., it is preferable to add a slight amount or a small amount of at least one kind of substance selected from a group consisting of nitroalkanes, ethers, epoxides, and amines as a stabilizer for preventing such a reaction. Further, in the present cleaning solvent, it is preferable to add a slight amount or a small amount of perfume such as d-limonene to control the odor of NPB.

[0023] Similarly, as for 1,1,1,3,3-pentafluorobutane, if the object to be cleaned is made of iron, zinc, aluminum, copper,

brass, etc. when it is used for cleaning in a heated state or as steam, there are cases in which it becomes unstable because of an influence caused by the metal. Therefore, it is preferable to add, as a stabilizer, at least one kind of compound selected from nitro compounds, phenols, amines, ethers, amylenes, epoxides, or triazoles. Specifically, as stabilizers, there are: epoxides such as propylene oxide, 1,2-butylene oxide, and glycidol; phosphites such as dimethyl phosphite, diisopropyl phosphite, and diphenyl phosphite; thiophosphites such as trilauryl trichlorophosphite; phosphine sulphides such as triphenoxyposphine sulphide and trimethylphosphine sulphide; boron compounds such as boric acid, triethyl borate, triphenyl borate, phenylboronic acid, and diphenylboronic acid; phenols such as 2,6-di-tert-butyl-para-cresol; nitroalkanes such as nitromethane and nitroethane; acrylic esters such as methyl acrylate and ethyl acrylate; and also, dioxane, tert-butanol, pentaerythritol, and para-isopropenyl toluene. As for the amount of addition of these stabilizers, it is preferable to set the amount to 0.01 through 5 wt% of the whole amount of the solvent composition for cleaning, although the amount is not to be particularly limited.

[0024] On the other hand, it is possible to list, for example, the following as alkanes with a carbon number of 5 or more and cycloalkanes with a carbon number of 5 or more, but they are not limited to these: pentane, 2-methyl butane, 2,2-dimethyl propane, hexane, 2-methyl pentane, 3-methyl pentane, 2,2-dimethyl butane, 2,3-dimethyl butane, heptane, 2-methyl hexane, 3-methyl hexane, 2,3-dimethyl pentane, 2,4-dimethyl pentane, octane, 2,2,3-trimethyl pentane, 2,2,4-trimethyl pentane, cyclopentane, methyl cyclopentane, cyclohexane, methyl cyclohexane, and ethyl cyclohexane. Further, alcohols include, for example: methanol, ethanol, i-propanol, n-propanol, n-butanol, i-butanol, s-butanol, and t-butanol. As regards the alkanes with a carbon number of 5 or more, the cycloalkanes with a carbon number of 5, and the alcohols, one kind of solvent may be mixed, or a mixed solvent containing two kinds or more of them may be mixed.

[0025] Furthermore, as regards nitromethane, nitroethane, d-limonene, and 3-methoxybutyl acetate, at least one kind of solvent selected from the above may be mixed, and it is also needless to say that two kinds or more of the above may be mixed.

[0026] As main applications of the solvent composition for cleaning according to the present invention, it is possible to name: resist removing agents, flux cleaners, degreasing cleaners for oils and fats etc., buffing cleaners, solvents for

dry cleaning, removing agents for grease, oil, wax, ink etc., solvents for paint, extractants, cleaners for various articles made of glass, ceramics, rubber, metal etc. and particularly for IC parts, electrical equipments, precision equipments, optical lenses, etc., or water removing agents.

Further, as for the cleaning method to which the solvent composition for cleaning according to the present invention can be applied, there are, for example, manual wiping, immersion, spraying, shaking, ultrasonic cleaning, and steam cleaning.

Next, various tests that were carried out for confirming the performance of the solvent composition for cleaning according to the present invention are described below.

<< Machine Oil Cleaning Test >> In this test, test pieces made of SUS-304 (length 25 mm x width 30 mm x thickness 2 mm) were prepared, and, after immersing these test pieces into machine oil (CQ-30: made by Nippon Oil Co., Ltd.), they were immersed into each cleaning fluid for approximately 3 minutes. After subjecting the test pieces to a drying process, the cleansing state of the test pieces was studied. Cleaning fluids obtained by mixing each of normal propyl bromide (NPB), isopropyl bromide (IPB), nitromethane, nitroethane, d-limonene, and 3-methoxybutyl acetate (3-MBA) to 1,1,1,3,3-pentafluorobutane (365mfc) were used. The following table 1 through table 3 summarize the composition of each cleaning fluid and the results of cleaning. It should be noted that a small amount of nitroethane is mixed, as a stabilizer, to the cleaning fluid to which normal propyl bromide (NPB) or isopropyl bromide (IPB) is mixed.

[0030]

[Table 1]

Machine Oil Cleaning Test 1 (365mfc - NPB)

	A	B	C	D	E	F	G	H	I	J
365mfc (wt%)	100	90	85	80	75	70	65	60	50	40
NPB (wt%)	0	10	15	20	25	30	35	40	50	60
Cleaning results	x	x	x	o	o	o	o	o	o	o

x: small cleaning effect o: satisfactory @: extremely good

365mfc: 1,1,1,3,3-pentafluorobutane (C₄H₉F₅)

NPB: normal propyl bromide

[Table 2]

Machine Oil Cleaning Test 2 (365mfc - IPB)

	A	B	C	D	E	F	G	H	I	J
365mfc (wt%)	100	90	85	80	75	70	65	60	50	40
IPB (wt%)	0	10	15	20	25	30	35	40	50	60
Cleaning results	x	x	x	o	o	o	o	o	o	o

x: small cleaning effect o: satisfactory @: extremely good

365mfc: 1,1,1,3,3-pentafluorobutane (C₄H₉F₅)

IPB: isopropyl bromide

[Table 3]

Machine Oil Cleaning Test 3

(365mfc, nitroethane, nitromethane, d-limonene)

	365mfc (wt%)	nitroethane (wt%)	nitromethane (wt%)	d-limonene (wt%)	3-MBA (wt%)	Cleaning ability
A	80	20	—	—	—	x
B	75	25	—	—	—	x
C	70	30	—	—	—	o
D	65	35	—	—	—	o
E	60	40	—	—	—	o
F	50	50	—	—	—	o
G	80	—	20	—	—	x
H	75	—	25	—	—	x
I	70	—	30	—	—	o
J	65	—	35	—	—	o
K	60	—	40	—	—	o
L	50	—	50	—	—	o
M	80	—	—	20	—	x
N	75	—	—	25	—	x
O	70	—	—	30	—	o
P	65	—	—	35	—	o
Q	60	—	—	40	—	o
R	50	—	—	50	—	o
S	80	—	—	—	20	x
T	75	—	—	—	25	x
U	70	—	—	—	30	o
V	65	—	—	—	35	o
W	60	—	—	—	40	o
Y	50	—	—	—	50	o

o: satisfactory x: small cleaning effect

365mfc: 1,1,1,3,3-pentafluorobutane (C₄H₉F₅)

3-MBA: 3-methoxybutyl acetate

[0031] From these test results, it has been found that, in terms of cleaning machine oil, it is necessary to include, with respect to 1,1,1,3,3-pentafluorobutane (365mfc), 20 wt% or more of normal propyl bromide or isopropyl bromide, and 30 wt% or more of nitromethane, nitroethane, d-limonene, or 3-methoxybutyl acetate.

[0032] << Flux Cleaning Test >> In this test, flux (TAMURA P-AL-4 made by TAMURA corporation) was applied to the whole surface of a printed wiring board for testing, and, after subjecting it to a burning process in an electric furnace at approximately 200 °C for approximately 2 minutes, it was immersed into a cleaning fluid for approximately 3 minutes. Then, after subjecting the printed wiring board to a drying process, the cleansing state was examined. Cleaning fluids obtained by mixing each of normal propyl bromide (NPB), isopropyl bromide (IPB), nitromethane, nitroethane, d-limonene, and 3-methoxybutyl acetate (3-MBA) to 1,1,1,3,3-pentafluorobutane (365mfc) were used. The following table 4 through table 6 summarize the composition of each cleaning fluid and the results of cleaning. It should be noted that a small amount of nitroethane is mixed, as a stabilizer, to the cleaning fluid to which normal propyl bromide (NPB) or isopropyl bromide (IPB) is mixed.

[0033]

[Table 4]

Flux Cleaning Test 1 (365mfc - NPB)

	A	B	C	D	E	F	G	H	I	J
365mfc (wt%)	100	90	80	70	65	60	55	50	40	30
NPB (wt%)	0	10	20	30	35	40	45	50	60	70
Cleaning results	x	x	x	x	O	⊙	⊙	⊙	⊙	⊙

x: small cleaning effect O: satisfactory ⊙: extremely good
365mfc: 1,1,1,3,3-pentafluorobutane (C₄H₉F₅)
NPB: normal propyl bromide

[Table 5]

Flux Cleaning Test 2 (365mfc - IPB)

	A	B	C	D	E	F	G	H	I	J
365mfc (wt%)	100	90	80	70	65	60	55	50	40	30

IPB (wt%)	0	10	20	30	35	40	45	50	60	70
Cleaning results	x	x	x	x	O	⊙	⊙	⊙	⊙	⊙

x: small cleaning effect O: satisfactory ⊙: extremely good
365mfc: 1,1,1,3,3-pentafluorobutane (C₄H₉F₅)
IPB: isopropyl bromide

[Table 6]

Flux Cleaning Test 3

(365mfc, nitroethane, nitromethane, d-limonene, 3-MBA)

	365mfc (wt%)	nitroethane (wt%)	nitromethane (wt%)	d-limonene (wt%)	3-MBA (wt%)	Cleaning ability
A	80	20	—	—	—	x
C	70	30	—	—	—	x
D	65	35	—	—	—	x
E	60	40	—	—	—	O
E	50	50	—	—	—	O
F	40	60	—	—	—	O
G	30	70	—	—	—	O
H	20	80	—	—	—	O
I	80	—	20	—	—	x
J	70	—	30	—	—	x
K	65	—	35	—	—	x
L	60	—	40	—	—	O
M	50	—	50	—	—	O
N	40	—	60	—	—	O
O	30	—	70	—	—	O
P	20	—	80	—	—	O
Q	80	—	—	20	—	x
R	70	—	—	30	—	x
S	65	—	—	35	—	x
T	60	—	—	40	—	O
U	50	—	—	50	—	O
V	40	—	—	60	—	O
W	30	—	—	70	—	O
X	20	—	—	80	—	O
Y	10	—	—	90	—	O
Z	5	—	—	95	—	O
AA	80	—	—	—	20	x
AB	70	—	—	—	30	x
AC	65	—	—	—	35	x
AD	60	—	—	—	40	O
AE	50	—	—	—	50	O

AF	40	—	—	—	—	60	○
AG	30	—	—	—	—	70	○
AH	20	—	—	—	—	80	○
AI	10	—	—	—	—	90	○

O: satisfactory	X: small cleaning effect
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365mfc: 1,1,1,3,3-pentafluorobutane (C₄H₂F₅)

3-MBA: 3-methoxybutyl acetate

[0034] From these test results, it has been found that, in terms of cleaning flux, it is necessary to include, with respect to 1,1,1,3,3-pentafluorobutane (365mfc), 35 wt% or more of normal propyl bromide (NPB) or isopropyl bromide (IPB), and 40 wt% or more of nitromethane, nitroethane, d-limonene, or 3-methoxybutyl acetate (3-MBA).

[0033] << Influence on plastics, Rubbers, Etc. >>
Tests for examining the influence of the solvent on various kinds of plastics, rubbers, etc. were carried out. In these tests, soft vinyl chloride, hard vinyl chloride, polycarbonate (PC), acrylic resin, nylon 66 (registered trademark), polyacetal, polyurethane resin, phenolic resin, epoxy resin, melamine resin, urea resin, polyethylene, and polypropylene were prepared as the plastics, fluoro rubber, chloroprene rubber, silicone rubber, urethane rubber, SBR, natural rubber, and butyl rubber were prepared as the rubbers, and a test of immersing each of them into the cleaning fluid for approximately 6 hours at room temperature was carried out. Then, a drying process was performed and the presence or absence of influence was studied.

[0036]

[Table 7]

Influence on Plastics, Rubbers, Etc. 1 (365mc, NPB, IPB)

[illegible]

11

[illegible]

O : no influence X : having influence

165mfc: 1,1,1,3,3-pentafluorobutane ($C_4H_3F_5$)

NPA: normal propyl bromide

1. **ВВЕДЕНИЕ**
 2. **ОБЪЕКТ И ПРЕДМЕТ ИССЛЕДОВАНИЯ**
 3. **ЦЕЛИ И ЗАДАЧИ ИССЛЕДОВАНИЯ**
 4. **МЕТОДЫ ИССЛЕДОВАНИЯ**
 5. **РЕЗУЛЬТАТЫ ИССЛЕДОВАНИЯ**
 6. **ЗАКЛЮЧЕНИЕ**
 7. **СПИСОК ЛИТЕРАТУРЫ**
 8. **ПРИЛОЖЕНИЯ**
 9. **УКАЗАТЕЛЬ**
 10. **ДОПОЛНИТЕЛЬНЫЕ МАТЕРИАЛЫ**

[Table 8]

Influence on Plastics, Rubbers, Etc. 2

(365mg. nitroethane, nitromethane)

(365mfc, nitroethane, nitromethane)											
	A	B	C	D	E	F	G	H	I	J	
365mfc (wt%)	70	60	50	40	30	70	60	60	40	30	
nitroethane (wt%)	30	40	50	60	70	—	—	—	—	—	
nitromethane (wt%)	—	—	—	—	—	30	40	50	60	70	
vinyl chloride (soft)	○	○	○	x	x	○	○	x	x	x	
vinyl chloride (hard)	○	○	○	x	x	○	○	x	x	x	
polycarbonate	○	○	○	○	○	○	○	○	○	○	
acrylic resin	○	○	○	○	○	○	○	○	○	○	
nylon 88	○	○	○	○	○	○	○	○	○	○	
polyacetal	○	○	○	○	○	○	○	○	○	○	
polyurethane resin	○	○	○	○	○	○	○	○	○	○	
phenolic resin	○	○	○	○	○	○	○	○	○	○	
epoxy resin	○	○	○	○	○	○	○	○	○	○	
melamine resin	○	○	○	○	○	○	○	○	○	○	
urea resin	○	○	○	○	○	○	○	○	○	○	
polyethylene	○	○	○	○	○	○	○	○	○	○	
polypropylene	○	○	○	○	○	○	○	○	○	○	
fluoro rubber	○	○	○	○	○	○	○	○	○	○	
chloroprene rubber	○	○	○	x	○	○	○	○	x	○	
silicone rubber	○	○	○	○	○	○	○	○	○	○	
urethane rubber	○	○	○	○	○	○	○	○	○	○	
SBR	○	○	○	○	○	○	○	○	○	○	
natural rubber	○	○	○	○	○	○	○	○	○	x	
butyl rubber	○	○	○	○	○	○	○	○	x	x	

Q	: no influence	X: having influence
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365mg; 1,1,1,3,3-pentafluorobutane (C₄H₃F₅)

[Table 9]

12

Influence on Plastics, Rubbers, Etc. 3
(365mfc, d-limonene, 3-MBA)

	A	B	C	D	E	F	G	H	I	J
365mfc (wt%)	70	60	50	40	30	70	60	50	40	30
d-limonene (wt%)	30	40	50	60	70	—	—	—	—	—
3-MBA (wt%)	—	—	—	—	—	30	40	50	60	70
vinyl chloride (soft)	O	O	O	X	X	O	O	X	X	X
vinyl chloride (hard)	O	O	O	X	X	O	O	X	X	X
polycarbonate	O	O	O	O	O	O	O	O	O	O
acrylic resin	O	O	O	O	O	O	O	O	O	O
nylon 88	O	O	O	O	O	O	O	O	O	O
polyacetal	O	O	O	O	O	O	O	O	O	O
polyurethane resin	O	O	O	O	O	O	O	O	O	O
phenolic resin	O	O	O	O	O	O	O	O	O	O
epoxy resin	O	O	O	O	O	O	O	O	O	O
melamine resin	O	O	O	O	O	O	O	O	O	O
urea resin	O	O	O	O	O	O	O	O	O	O
polyethylene	O	O	O	O	O	O	O	O	O	O
polypropylene	O	O	O	O	O	O	O	O	O	O
fluoro rubber	O	O	O	O	O	O	O	O	O	O
chloroprene rubber	O	O	O	X	X	O	O	O	X	X
silicone rubber	O	O	O	O	O	O	O	O	O	O
urethane rubber	O	O	O	O	X	O	O	O	X	X
SBR	O	O	O	X	X	O	O	O	X	X
natural rubber	O	O	O	X	X	O	O	O	X	X
butyl rubber	O	O	O	O	O	O	O	O	O	O

O : no influence X : having influence

365mfc: 1,1,1,3,3-pentafluorobutane (C₄H₃F₅)

3-MBA: 3-methoxybutyl acetate

[0037] From these results, it was possible to confirm that in some cases, soft and hard vinyl chloride and polycarbonate are negatively affected. It was found that, if negative influence is to be kept from being exerted on soft vinyl chloride, hard vinyl chloride, and polycarbonate, then it is necessary to set the content of normal propyl bromide and isopropyl bromide to 45 wt% or less, and set the content of nitromethane, nitroethane, d-limonene, and 3-methoxybutyl acetate (3-MBA) to 50 wt% or less, with respect to 1,1,1,3,3-pentafluorobutane (365mfc).

<< Flammability Test >> In this test, a study was made on the relationship between flammability and the content for when 1,1,1,3,3-pentafluorobutane (365mfc) includes alkanes with a carbon number of 3 or more, cycloalkanes with a carbon number of 3 or more, or alcohols, because these solvents

have flammability and are combustibles. Ethyl alcohol (ethanol), methyl alcohol (methanol), and heptane were used as the solvents to be mixed. The following table 10 summarizes the test results. It should be noted that the flammability was studied according to the tag closed cup method.

[0039]

[Table 10]

Flammability Test 1

(365mfc, NPB, ethanol, methanol, heptane)

	365mfc (wt %)	NPB (wt %)	ethanol (wt %)	methanol (wt %)	heptane (wt %)	flamma- bility
A	80	20	0	—	—	no
B	77	20	3	—	—	no
C	75	20	5	—	—	no
D	72	20	8	—	—	no
E	70	20	10	—	—	no
F	67	20	13	—	—	no
G	66	20	15	—	—	no
H	62	20	18	—	—	yes
I	60	20	20	—	—	yes
J	77	20	—	3	—	no
K	75	20	—	5	—	no
L	72	20	—	8	—	no
M	70	20	—	10	—	no
N	67	20	—	13	—	no
O	65	20	—	15	—	no
P	62	20	—	18	—	yes
Q	60	20	—	20	—	yes
R	77	20	—	—	3	no
S	75	20	—	—	5	no
T	72	20	—	—	8	no
U	70	20	—	—	10	no
V	67	20	—	—	13	no
W	65	20	—	—	15	no
X	62	20	—	—	18	yes
Y	60	20	—	—	20	yes

365mfc: 1,1,1,3,3-pentafluorobutane (C₄H₃F₅)

NPB: normal propyl bromide

[0040] From these results, it was found that, since flammability arises when 18 wt% or more of each solvent of ethyl alcohol, methyl alcohol, and heptane is contained, in order to keep the solvent composition for cleaning (type 2) according to the present invention from becoming flammable, it is

necessary to set the content of these solvents to 15 wt% or less. [0041] Further, since nitromethane, nitroethane, d-limonene, and 3-methoxybutyl acetate (3-MBA) similarly have flammability, the relationship between flammability and the content of these solvents was also studied. The following table 11 summarizes the test results. It should be noted that the flammability was measured according to the Tag closed cup method.

[0042]

[Table 11]

Flammability Test 2

(365mfc, nitroethane, nitromethane, d-limonene, 3-MBA)

	365mfc (wt %)	nitroethane (wt %)	nitromethane (wt %)	d-limonene (wt %)	3-MBA (wt %)	flamma- bility
A	70	30	—	—	—	no
B	60	40	—	—	—	no
C	50	50	—	—	—	no
D	40	60	—	—	—	no
E	30	70	—	—	—	no
F	20	80	—	—	—	yes
G	10	90	—	—	—	yes
H	70	—	30	—	—	no
I	60	—	40	—	—	no
J	50	—	50	—	—	no
K	40	—	60	—	—	no
L	30	—	70	—	—	no
M	20	—	80	—	—	no
N	10	—	90	—	—	yes
O	70	—	—	30	—	no
P	60	—	—	40	—	no
Q	50	—	—	50	—	no
R	40	—	—	60	—	no
S	30	—	—	70	—	no
T	20	—	—	80	—	no
U	10	—	—	90	—	no
V	5	—	—	95	—	yes
W	70	—	—	—	30	no
Y	60	—	—	—	40	no
Z	50	—	—	—	50	no
AA	40	—	—	—	60	no
AB	30	—	—	—	70	no
AC	20	—	—	—	80	no
AD	10	—	—	—	90	no
AE	5	—	—	—	95	yes

365mfc: 1,1,1,3,3-pentafluorobutane ($C_4H_2F_5$)
3-MBA: 3-methoxybutyl acetate

[0043] From these results, it was found that, since flammability arises when 80 wt% or more of nitromethane or nitroethane is contained, and 95 wt% or more of d-limonene or 3-methoxybutyl acetate (3-MBA) is contained, in order to keep the solvent composition for cleaning (type 3) according to the present invention from becoming flammable, it is necessary to set the content of nitromethane and nitroethane to 70 wt% or less, and the content of d-limonene and 3-methoxybutyl acetate (3-MBA) to 90 wt% or less.

[0044] << Metal Corrosion Test >> In this test, according to JIS-K1600, aluminum pieces (JIS-H-4000, Al100P) were arranged in both the liquid phase portion and the gas phase portion of the cleaning fluid after cleaning, and the state of corrosion of metal after approximately 48 hours was studied.

[0045]

[Table 12]

Metal Corrosion Test 1 (365mfc, NPB, IPB)

	A	B	C	D	E	F	G	H	I	J	K	L
365mfc (wt%)	80	70	60	50	40	30	80	70	60	50	40	30
NPB (wt%)	20	30	40	50	60	70	—	—	—	—	—	—
IPB (wt%)	—	—	—	—	—	—	20	30	40	50	60	70
results	O	O	O	O	O	O	O	O	O	O	O	O

X : corrosion O : no corrosion

365mfc: 1,1,1,3,3-pentafluorobutane ($C_4H_2F_5$)

NPB: normal propyl bromide

IPB: isopropyl bromide

[Table 13]

Metal Corrosion Test 2

(365mfc, nitroethane, nitromethane, d-limonene, 3-MBA)

	365mfc (wt %)	nitroethane (wt %)	nitromethane (wt %)	d-limonene (wt %)	3-MBA (wt %)	results
A	70	30	—	—	—	O
B	60	40	—	—	—	O
C	50	50	—	—	—	O
D	40	60	—	—	—	O

contains 1,1,1,3,3-pentafluorobutane as a main ingredient and that is superior in cleaning ability.
[Means for Resolution] Normal propyl bromide, isopropyl bromide, nitromethane, nitroethane, d-limonene, or 3-methoxybutyl acetate is mixed to 1,1,1,3,3-pentafluorobutane. Further, to the above, at least one kind of solvent selected from among alkanes with a carbon number of 5 or more, cycloalkanes with a carbon number of 5 or more, or alcohols is mixed.

Continued from Front Page

(38) Field of Search (Int. Cl.⁷, DB name)

C11D 7/50

C23G 5/028

H01L 21/304 647

CA (STN)

CAOLD (STN)

CAPLUS (STN)

REGISTRY (STN)

(10) 日本国特許庁 (JP) (12) 特許公報 (B1)

(11) 特許番号
特許第3263065号
(P3263065)

(15) 発行日 平成14年3月4日 (2002.3.4) (20) 登録日 平成15年12月21日 (2003.12.21)

(5) Int. Cl.	発明の分野
F1	
C11D 7/50	
C23C 5/028	
H01L 21/304	647A

特許の範囲 (全 12 図)

(21) 出願番号	特許第2001-37650(P2001-37650)	(73) 特許権者	株式会社カネコ化学
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特許審判請求日		審査官	近藤 政寛
(56) 参考文献	特開 平6-220494 (JP, A) 特開 平11-50087 (JP, A) 特開 平9-111032 (JP, A) 特開 平5-140592 (JP, A) 特開 平5-158292 (JP, A) 国際公開09/58833 (WO, A1)		

(54) 発明の名称 洗浄用剤組成物

(57) 特許請求の範囲
【請求項1】 (a) 1, 1, 1, 1, 3, 3-ペンタフル
オロブタンを30〜70重量%、(b) ニトロメタン、
ニトロエタン、d-リネン及び3-メトキシ-ブチル
アセテートの中から選ばれた1種の溶剤または2種以上
の混合溶剤を30〜70重量%、含有することを特徴と
する洗浄用剤組成物。

【発明の詳細な説明】

【0001】
【発明の属する技術分野】 本発明は、1, 1, 1, 3, 3-ペンタフルオロブタンを主成分とする洗浄用剤組成物に
関する。特にその洗浄能力をアップする技術に
関する。

【0002】

【従来の技術】 従来、塩素系溶剤やフッ素系溶剤がフ

ラックス洗剤、ドライクリーニング用洗剤、脱脂洗
剤、パワークリーナー、レジスト剥離剤または付着除去
剤などとして広く使用されてきた。しかしながら、
塩素系溶剤は地下水汚染の原因物質として、またフッ
素系溶剤はオゾン層破壊の原因物質として、いずれも環
境上の問題からその使用は規制されつつある。そこで、
かかる溶剤にかわる新規の溶剤が各方面で要請されて
いる。

【0003】 その1つに、1, 1, 1, 3, 3-ペンタフル
オロブタン (368 m²、化学式: C₅H₈F₈)
がある (特開 平5-171189号、特開 平5-171
190号、特開 平6-322394号、特開 平7-18
8700号等参照)。1, 1, 1, 3, 3-ペンタフル
オロブタンは、その分子構造中に塩素を含まずオゾン破
壊係数 (ODP) は0であり、毒性も少なく、また環境

化係数 (GWP) も小さく、環境に優しくクリーンであ
るという優れた特徴を有している。

【0004】

【発明が解決しようとする課題】 しかしながら、1,
1, 1, 3, 3-ペンタフルオロブタン (368 m²)
c) は、K₂B₂ (カクリブナール) が約1.4とさ
めて低く、ほとんど脱脂能力がないという問題があ
つた。K₂B₂値が低いと、各種洗剤としては、十分な洗
浄能力を有することはできない。

【0005】 そこで、1, 1, 1, 3, 3-ペンタフル
オロブタンに対し、これよりもK₂B₂値の高い脱脂能力
のある塩化メチレン、又は、1, 1-ジクロロ-1-フル
オロエタン (HCFC141b) を混合して、洗浄能力
のアップを図ることが提案されている (特開 平5-17
1189号および特開 平11-162232号公報参
照)。

【0006】 しかしながら、塩化メチレンは、毒性が強
いことから、作業時の人体への悪影響が懸念されること
から、使用上望ましくはないとともに、今後使用が厳し
くなりつつある。また、1, 1-ジクロロ-1-フルオ
ロエタン (141b) は、オゾン破壊係数が高く、今
後、規制の対象とならねない。

【0007】 本発明は、このような事情に鑑みてなされ
たものであって、その目的は、1, 1, 1, 3, 3-ペ
ンタフルオロブタンを主成分とする洗剤組成物、特に脱脂
洗浄能力に優れた洗浄用剤組成物を提供することにあ
る。

【0008】

【課題を解決するための手段】 このような目的を達成す
るために本発明に係る洗浄用剤組成物にあっては、
(a) 1, 1, 1, 3, 3-ペンタフルオロブタンを3
0〜70重量%、(b) ニトロメタン、ニトロエタン、
d-リネン及び3-メトキシ-ブチルアセテートの中
から選ばれた1種の溶剤または2種以上の混合溶剤を3
0〜70重量%、含有することを特徴とする。

【0009】

【0010】

【0011】

【0012】

【0013】

【0014】

【0015】

【0016】 ニトロメタン、ニトロエタン、d-リネ
ンおよび3-メトキシ-ブチルアセテートは、本発明
に係る洗浄用剤組成物にあっては、1, 1, 1, 3, 3-ペン
タフルオロブタンに対して、洗浄能力をアップさせる
のに相応しい溶剤として選出されたものである。これら
は、脱脂洗浄能力として十分な性能を有する。

【0017】 1, 1, 1, 3, 3-ペンタフルオロブ
タンを30〜70重量%、ニトロメタン、ニトロエタン、

d-リネン及び3-メトキシ-ブチルアセテートの中
から選ばれた1種の溶剤または2種以上の混合溶剤を3
0〜70重量%と配合したものは、洗浄能力が向上する
とあり洗浄能力のアップが不十分で、十分な洗浄効果を
得ることができないとともに、含有量が少なくなる
は、ニトロメタン、ニトロエタン、d-リネン及び3-
メトキシ-ブチルアセテートの特性が大きく現れ、
1, 1, 1, 3, 3-ペンタフルオロブタンの優れた特
性が生かされなくなりかねない。

【0018】

【発明の実施の形態】 以下に本発明に係る洗浄用剤組成
物の実施形態について説明する。本発明に係る洗浄
用剤組成物は、(a) 1, 1, 1, 3, 3-ペンタフル
オロブタンを30〜70重量%、(b) ニトロメ
タン、ニトロエタン、d-リネン及び3-メトキシ-ブ
チルアセテートの中から選ばれた1種の溶剤または2種
以上の混合溶剤を30〜70重量%、含有する。この
他、次の2つのタイプの洗浄用剤組成物についても本
発明と関係し、洗浄能力に優れた組成物を得ることが
できる。

【0019】 (a) 1, 1, 1, 3, 3-ペンタフル
オロブタンを30〜80重量%、(b) ノルマルブ
ロピルプロピド及び/又はイソプロピルプロピドを
20〜70重量%、含有する。
【0020】 (a) 1, 1, 1, 3, 3-ペンタフル
オロブタンを27〜80重量%、(b) ノルマルブ
ロピルプロピド及び/又はイソプロピルプロピドを
20〜70重量%、(c) 炭素数6個以上のアルカン
類、炭素数8個以上のシクロアルカン類、アルコール類
から選ばれた1種の溶剤または2種以上の混合溶剤を8
〜15重量%、含有する。

【0021】

【0022】 ノルマルブロピルプロピド (別称: n-
プロピルプロピド、1-ブチルプロピド、以下単にNPBと
いう) およびイソブチルプロピド (別称: 異化イ
ソブチルプロピド、2-ブチルプロピド、以下IPBとい
う) は、1, 1, 1, 3, 3-ペンタフルオロブタンの
洗浄能力をアップさせるのに相応しい溶剤として選出
されたものである。これらNPBおよびIPBは、K₂B₂値が
1.25と比較的低く、脱脂洗浄に優れている。その上、
1, 1, 1, 3, 3-ペンタフルオロブタンと同様、
毒性がなく不燃または難燃な性質を有しているため、
使用に際しては、安全で取り扱いやすいとともに、その分
子構造中に塩素やフッ素を含まず、オゾン破壊係数 (O
DP) も低減化係数 (GWP) も小さく、環境に優しい
クリンであるという優れた特性を有している。これら
K₂B₂値の高いNPB及び/又はIPBは、1, 1, 1, 3, 3-
ペンタフルオロブタンに混合することで、脱脂
能力、特に脱脂洗浄能力の大幅なアップが図れ、各種溶
剤としては、十分な性能を有することができ、

金属食試験2(365mle, ニトロエタン, ニトロメタン, d-リモノン, 3-MBA)

	365mle (重量%)	ニトロエタン (重量%)	ニトロメタン (重量%)	d-リモノン (重量%)	3-MBA (重量%)	結果
A	70	30	—	—	—	—
B	60	40	—	—	—	—
C	50	50	—	—	—	—
D	40	60	—	—	—	—
E	30	70	—	—	—	—
F	70	—	30	—	—	—
G	60	—	40	—	—	—
H	50	—	50	—	—	—
I	40	—	60	—	—	—
J	30	—	70	—	—	—
K	70	—	—	30	—	—
L	60	—	—	40	—	—
M	50	—	—	50	—	—
N	40	—	—	60	—	—
O	30	—	—	70	—	—
P	70	—	—	—	30	—
Q	60	—	—	—	40	—
R	50	—	—	—	50	—
S	40	—	—	—	60	—
T	30	—	—	—	70	—

x: 炭素含有リ O: 炭素無し
365mle: 1, 1, 1, 3, 3-ペンタフルオロプロパン(C₃H₂F₈)
3-MBA: 3-メチルブチルアセテート

- [0046] これらの結果、本発明に係る洗浄用溶剤組成物は、ニトロメタン及びニトロエタンについては80重量%以上、またd-リモノン及び3-メチルブチルアセテート(3-MBA)については、本発明で規定している含有量の範囲内でも引火性は生じない。
- [0047] 《まとめ》これらの試験結果をまとめると次のようなことが認められる。
- (1) 炭素油洗浄剤使用するためには、ノルマルプロピルプロピドまたはイソプロピルプロピドについては少なくとも20重量%以上、ニトロメタン、ニトロエタン、d-リモノンまたは3-メチルブチルアセテート(3-MBA)については少なくとも30重量%以上、含有している必要がある。
- (2) フラックス洗浄剤使用するためには、ノルマルプロピルプロピドまたはイソプロピルプロピドについては少なくとも35重量%以上、ニトロメタン、ニトロエタン、d-リモノンまたは3-メチルブチルアセテート(3-MBA)については少なくとも40重量%以上、含有している必要がある。
- [0048] (3) 炭素油化ドニールや炭素油化ドニール、ポリカーボネートに溶解性を与えるのを回避する場合には、ノルマルプロピルプロピドまたはイソプロピルプロピドの含有量を48重量%以下に、またニトロメタン、ニトロエタン、d-リモノンまたは3-メチルブチルアセテート(3-MBA)の含有量を50重量%以下に抑える。
- (4) 炭素油5個以上のアルカン類、炭素油5個以上のシクロアルカン類またはアルコール類を混合しても引火性が生じないようにするためには、その含有量を15重量%以下に設定する。
- (5) ニトロメタン及びニトロエタンについては80重量%以上、またd-リモノン及び3-メチルブチルアセテート(3-MBA)については、本発明で規定している含有量の範囲内でも引火性は生じない。
- (6) 本発明に係る洗浄用溶剤組成物では、金属に腐食等の影響を及ぼす心配がない。
- [0049] これらの事項を踏まえると、さらに好ましい組成成分の含有量の範囲は次のようになる。
- [1'] (a) 1, 1, 1, 3, 3-ペンタフルオロプロピド及び/又はイソプロピルプロピドを35~45重量%、含有することを特徴とする洗浄用溶剤組成物。
- [2'] (a) 1, 1, 1, 3, 3-ペンタフルオロプロピド及び/又はイソプロピルプロピドを35~45重量%、(b) ノルマルプロピルプロピド及び/又はイソプロピルプロピドを35~45重量%、(c) 炭素油5個以上のアルカン類、炭素油5個以上のシクロアルカン類、アルコール類から選ばれた1種の溶剤または2種以上の混合溶剤を3~15重量%、含有することを特徴とする洗浄用溶剤組成物。
- [3'] (a) 1, 1, 1, 3, 3-ペンタフルオロプロピド及び/又はイソプロピルプロピドを35~45重量%、(b) ノルマルプロピルプロピド及び/又はイソプロピルプロピドを35~45重量%、(c) 炭素油5個以上のアルカン類、炭素油5個以上のシクロアルカン類、アルコール類から選ばれた1種の溶剤または2種以上の混合溶剤を3~15重量%、含有することを特徴とする洗浄用溶剤組成物。
- [4] 炭素油5個以上のアルカン類、炭素油5個以上のシクロアルカン類またはアルコール類を混合しても引火性が生じないようにするためには、その含有量を15重量%以下に設定する。
- [5] 1, 1, 1, 3, 3-ペンタフルオロプロピドに對し

て、ニトロメタン、ニトロエタン、d-リモノン、3-メチルブチルアセテートを含有すること、洗浄能力、特に脱脂洗浄能力を大幅にアップさせることができ、各溶剤の引火性は十分な性能を確保させることができる。しかも、引火性がなくから危険物に該当しないから、安全で取り扱い易いとともに、オゾン層破壊係数(ODP)及び温暖化係数(GWP)も小さく、環境に優しくグリーンである。

[0051]
[0052]
[要約]

フロントページの続き

(58)調査した分野(Int. Cl.⁷, DB名)

C10 7/50
C23 5/028
H01 21/204 847
CA (STN)
CAOLD (STN)
CAPLUS (STN)
REGISTRY (STN)

[図1] 1, 1, 1, 3, 3-ペンタフルオロプロピドを主成分とする洗浄能力に優れた洗浄用溶剤組成物の組成。

[図2] 1, 1, 1, 3, 3-ペンタフルオロプロピド、ニトロメタン、ニトロエタン、d-リモノン、3-メチルブチルアセテートを混合する。またさらに、これらに炭素油5個以上のアルカン類、炭素油5個以上のシクロアルカン類またはアルコール類から選ばれた少なくとも1種の溶剤を混合する。

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